

# Performance Characteristics of Lithium Ion Cells at Low Temperatures

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## ABSTRACT

The low temperature charge and discharge characteristics of experimental MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cells containing different electrolytes were investigated. The use of low ethylene carbonate (EC)-content electrolyte formulations has resulted in good discharge performance to temperatures as low as -40°C. The effect of charge voltage and charge current upon the individual electrode potentials at low temperature was investigated using the three electrode cells (containing lithium reference electrodes). In some cases, lithium plating was observed to occur upon low temperature charge, and found to be facilitated by high charge voltages, high charge currents, and poor anode kinetics. Electrochemical characterization of the cells has helped to establish the conditions under which lithium plating can occur by providing information regarding the polarization effects present at each electrode.

## Introduction

In order to enable the operation of lander and rover vehicles on the surface of Mars, NASA requires long life, high energy density rechargeable batteries. The most recent mission to Mars involving surface operation using a rechargeable battery coupled with a solar array was the 1997 Mars Sojourner Lander, which employed a Silver-Zinc battery. The Ag-Zn battery was successful in providing power for the required 30 sols (battery was operational for ~ 65 sols). Although successful, silver-zinc technology is characterized by relatively poor cycle life performance (>100 cycles), poor low temperature performance (only > -10°C), and poor storage characteristics. Many future missions desire (or require) energy storage devices with higher specific energy, longer cycle life performance, and better low temperature performance. Lithium-ion battery technology has been identified by JPL/NASA as an attractive alternative to silver-zinc and is currently being used for the 2003 Mars Exploration Rovers (MER). In this mission, the battery is required to operate for 300 sols over a

wide temperature range (-20° to 40°C).<sup>1</sup> However, although current SOA lithium-ion technology is adequate, further improvements are desired to provide enhanced mission capability, such as improved low temperature performance (-40° to 40°C) and improved life characteristics (>3 years).

Thus, in recent years we have focused upon determining the technological viability of lithium-ion technology for future Mars missions and, in parallel, attempting to further develop the technology to meet more demanding mission requirements. The focus of our work has been upon: (1) developing advanced low temperature electrolytes, (2) studying the low temperature performance characteristics of lithium ion cells, (3) studying the effect of high temperature storage/exposure upon the low temperature performance capabilities (4) and identifying operational conditions which contribute to life limiting processes. In this paper, we would like to present some of our results obtained on experimental MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cells containing low temperature electrolytes. Specifically, we will discuss the low temperature discharge and charge characteristics, conditions

which may lead to lithium plating, and the impact of high temperature exposure upon the low temperature performance

## Experimental

For detailed electrochemical measurements and evaluation at low temperature, three-electrode, O-ring sealed, glass cells containing spiral rolls of MCMB electrodes,  $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  electrodes and lithium reference electrodes separated by two layers of porous polypropylene (Celgard 2500) were employed. The electrolyte solutions, consisting of carbonate solvents (EC, DMC, EMC and DEC) and dissolved  $\text{LiPF}_6$  salt, were purchased from Mitsubishi Chemicals (battery grade) with less than 50 ppm of water. Electrochemical measurements were made using an EG&G Potentiostat/Galvanostat interfaced with an IBM PC, using Softcorr 352. A Solartron 1255 Frequency Response Analyzer was used with this potentiostat for impedance measurements, using M388 software. Charge-discharge measurements and cycling tests were performed with an Arbin battery cyclier.

## Results and Discussion

### Low Temperature Discharge Characteristics

A number of factors affect the low temperature discharge (and charge) characteristics of lithium ion cells, most notably being the choice of electrolyte, the electrode loading, the particle size of active electrode materials, and cell design (i.e., tabing design, thermal properties, amount of electrolyte, etc.). Of all these factors, the most critical is the choice of electrolyte, since poor performance is obtained if the electrolyte has poor conductivity and/or freezes at low temperature. Thus, most of our efforts to improve the low temperature performance of lithium ion cells has been focused upon developing improved electrolytes which have high conductivity at low temperatures, and also possesses the requisite stability and compatibility with the electrode materials.

Past efforts at JPL have lead to identification of an electrolyte (1.0 M  $\text{LiPF}_6$

ethylene carbonate (EC) + diethyl carbonate (DEC) + dimethyl carbonate (DMC) (1:1:1))<sup>2,3</sup> which was demonstrated to provide good operation over a wide temperature range, good cycle life performance, and good storage.<sup>4,5</sup> Lithium-ion cell technology containing this electrolyte (Yardney Technology Products) have been baselined for use in 2003 MER<sup>1</sup> and have previously been developed and qualified for use in the Mars 2001 Surveyor Lander<sup>6</sup> (mission cancelled). In addition to advances made at JPL, other groups have developed electrolyte formulations with comparable performance, including work performed by the Army Research Lab. (resulting in 1.0 M  $\text{LiPF}_6$  EC+DMC+EMC (1:1:1))<sup>7</sup>, and efforts by Covalent Associates (1.0 M  $\text{LiPF}_6$  EC+EMC (1:3)).<sup>8</sup> Although these electrolyte solutions enable adequate operation at  $-20^\circ\text{C}$ , these formulations do not function well below  $-30^\circ\text{C}$ .

Recently we have reported that a number of electrolyte formulations containing low EC-content can enable efficient performance down to  $-40^\circ\text{C}$ .<sup>9</sup> As shown in Fig. 1, the choice of electrolyte can have a dramatic effect upon the discharge capacity delivered at low temperature. Although the previously identified electrolyte described above displayed negligible capacity in experimental MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells at  $-40^\circ\text{C}$ , a number low ethylene content electrolyte formulations were observed to have far superior performance enabling effective operation.

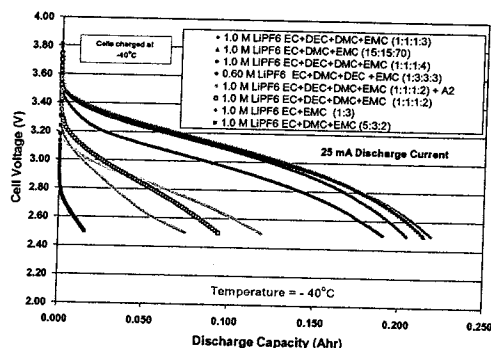
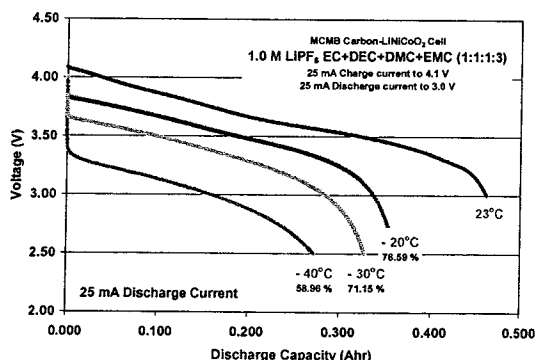


Fig. 1. Discharge capacity of MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cells with different electrolytes at  $-40^\circ\text{C}$  ( $\sim\text{C}/15$  rate to 2.75 V).

The electrolyte formulation which provided the best cell performance at low temperatures, 1.0 M LiPF<sub>6</sub> EC+DEC+DMC+EMC (1:1:1:3), delivered ~58% of the room temperature capacity at -40°C, as shown in Fig. 2. In addition, recent studies have shown that the



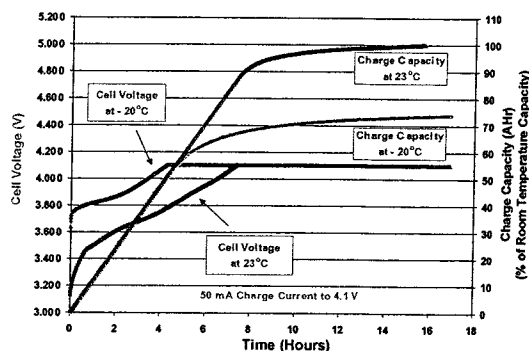
**Fig. 2.** Discharge capacity of MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cells at different temperatures (~C/15 rate to 2.75 V).

performance enhancement is even greater when the electrolyte is incorporated into prototype lithium ion cells (i.e., 9 Ahr DD-size cells provided by SAFT America, Inc.), where impressive capacity (> 70% of room temperature) and specific energy (> 85 Whr/Kg with a C/10 rate and room temperature charge) is delivered at -40°C.<sup>9</sup>

The improved low temperature performance observed with cells containing all carbonate mixtures with low EC-content electrolytes is due to the fact that they possess good conductivity at low temperatures and have good electrode passivating characteristics, producing protective, yet ionically conductive, electrode surface layers (or solid electrolyte interphase (SEI) layer), especially on carbon. It has been shown that although some candidate low temperature electrolytes display excellent conductivity at low temperature, they result in poor performance due to undesirable reactivity with the electrodes, producing resistive surface films leading to poor lithium kinetics.

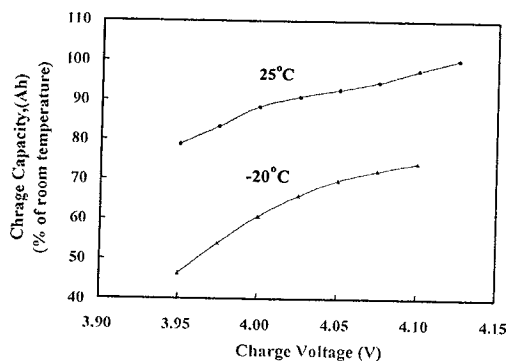
## Low Temperature Charge Characteristics

In general, the charge characteristics of lithium-ion cells are less facile than that of the discharge characteristics. Under constant current charging conditions, cells at low temperature are unable to accept a comparable amount of charge capacity compared to that which can be discharged at a similar rate, especially with high rates (>C/5). However, cells can be charged effectively at low temperature using modified constant current-constant potential charging methodologies. When such methods are employed at low temperatures, often a large portion of the charge capacity (and of the charge time) is obtained in the “taper mode” when the cell is held at constant potential (i.e., 4.1V), as illustrated in Fig. 3. As shown in Fig. 3, using an eight hour charge rate ~ 92% of full charge can be accepted by the cells at room temperature, whereas only ~ 73% of full capacity (% of room temperature) can be charge at -20°C.



**Fig. 3.** Charge characteristics of a MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cell with low EC-content electrolyte at -20°C (~C/8 rate to 4.1 V).

It is tempting to employ higher charge voltages at low temperatures to increase the charge capacity accepted. Indeed, as shown in Fig. 4, the effect of charge voltage at low temperatures is more dramatic than that at higher temperatures. However, charging at higher voltages (> 4.1V) can also be accompanied by undesirable reactions and/or processes, such as

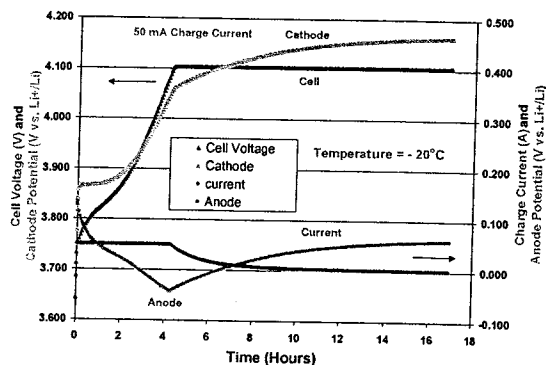


**Fig. 4.** Effect of charge voltage upon charge capacity of a large capacity prototype Li-ion cell at different temperatures ( $-20^{\circ}\text{C}$  and  $23^{\circ}\text{C}$ ).

lithium plating occurring at the anode (especially at high rates) and oxidative degradation of the electrolyte at high potentials at the cathode. The relative magnitude of both of these processes is dependent upon the degree of polarization observed at the anode compared with that of the cathode. To further elucidate these potential problems, it is helpful to analyze data obtained with cells containing reference electrodes, to enable monitoring of individual electrode potentials during charge.

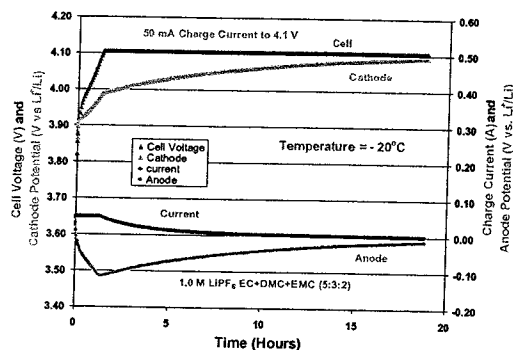
When a three-electrode MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell containing a low temperature electrolyte is charged at low temperature ( $-20^{\circ}\text{C}$ ) using a moderate rate ( $\sim \text{C}/8$ ), as shown in Fig. 5, it is apparent that the anode potential becomes negative versus the  $\text{Li}^+$  reference potential during a significant portion of the charge process. This is of concern, due to the fact that under these conditions lithium plating upon the electrode surface can occur, rather than the preferred lithium intercalation (or insertion) process into the carbon lattice structure. As shown in the figure, the point at which this is most severe is when the charge current and the charge voltage are the highest (occurring near the fourth hour of charge). It is somewhat unclear as to exactly how negative the anode potential must be to induce the competing plating reaction and whether any initially plated lithium is subsequently intercalated into the carbon structure during the taper mode of the charge process. In addition, the phenomenon

is further complicated by the fact different cell chemistries and/or different cell designs may behave differently depending upon relative polarization resistance of the anode compared with that of the cathode.



**Fig. 5.** Charge characteristics of a MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell with low EC-content electrolyte at  $-20^{\circ}\text{C}$  ( $\sim \text{C}/8$  rate to 4.1 V).

For example, when a similar MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell containing a different electrolyte is charged at low temperature under identical conditions, very different electrode potential profiles are obtained, as illustrated in Fig. 6.

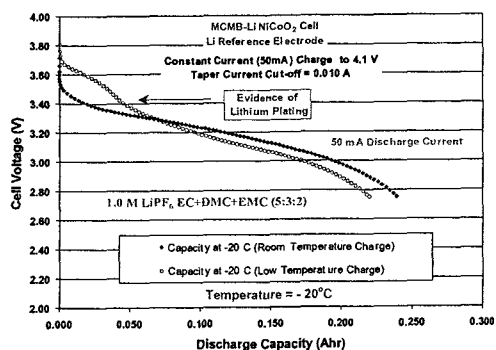


**Fig. 6.** Charge characteristics of a MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell at  $-20^{\circ}\text{C}$  with a poorly performing low temperature electrolyte.

As illustrated, the anode potential becomes much more negative under identical charge conditions ( $\sim 110 \text{ mV}$  vs.  $\text{Li}^+/\text{Li}$ ) compared to the previous cell described ( $\sim 50 \text{ mV}$  vs.  $\text{Li}^+/\text{Li}$ ), emphasizing that the electrolyte (and the corresponding film forming characteristics) can

have a dramatic effect upon cell behavior. In addition to becoming polarized to a greater extent, the anode potential in the second cell is never observed to become positive throughout the entire charge, suggesting more prevalent lithium plating can occur. These results suggest that the second cell described possesses poorer charge kinetics at the anode (presumably due to more resistive SEI film formation) compared with the cell containing the low-EC content low temperature electrolyte.

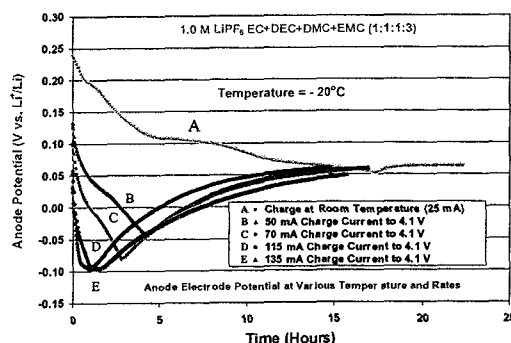
One method of determining whether lithium plating has indeed occurred as a result of the charge methodology employed at low temperature is by analyzing the voltage profile of the subsequent cell discharge. As shown in Fig. 7, when the cell containing the 1.0M  $\text{LiPF}_6$  EC+DMC+EMC (5:3:2) electrolyte is charged at



**Fig. 7.** Discharge profiles of a MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell at  $-20^\circ\text{C}$  (room temperature and low temperature charge comparison).

low temperature with a C/8 rate, the subsequent discharge charge is characterized by a much higher discharge voltage initially compared to the discharge obtained with a room temperature charge. This higher discharge voltage is most likely due to presence of a lithium stripping reaction which is characterized by a lower overpotential compared to that of the lithium de-intercalation process at the anode. The presence of lithium plating/stripping reactions is potentially very deleterious to cell health, due to the possibly of exposed metallic lithium reacting with electrolyte, resulting in net lithium loss, excessive SEI layer build-up on the electrode, and/or the possibility of pressure build-up in the cell due to electrolyte decomposition.

Although it is difficult to predict quantitatively how much lithium will be plated under any particular charge condition or cell chemistry, it is clear that the process is most prevalent when (1) high charge voltages are employed, (2) high charge rates are used, (3) short taper periods are used, (4) and when the anode is polarized to a much greater extent than that of the cathode at low temperature. For example, much more negative anode potentials are observed at low temperature when high charge currents are used, as shown in Fig. 8.



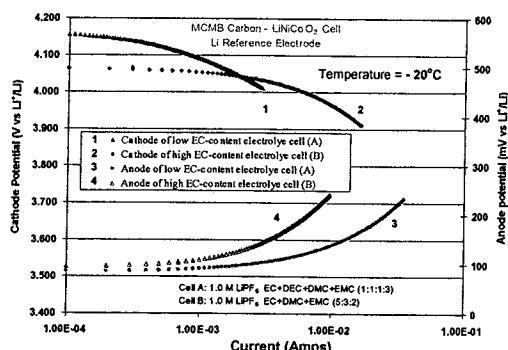
**Fig. 8.** Anode potential of a MCMB- $\text{Li}_x\text{Ni}_y\text{Co}_{1-y}\text{O}_2$  cell charged at  $23^\circ\text{C}$  (A) and  $-20^\circ\text{C}$  (B-E) using different charge currents.

Although the anode potential of the cell shown in Fig. 8 is observed to become much more negative ( $\sim 100\text{mV}$  vs.  $\text{Li}^+/\text{Li}$ ) when using high charge currents ( $>100\text{ mA}$  or C/4 rate), no evidence of lithium plating was observed upon analyzing the subsequent discharges of this cell. This suggests that although lithium may have been plated during the initial stages of the charge process (similar potential characteristics as seen in Fig. 6), the anode potential became sufficiently positive such that the desired lithium intercalation reaction can occur.

### Electrochemical Characterization

In order to more fully understand the cell performance characteristics which lead to the possibility of lithium plating occurring at low temperature, a number of electrochemical techniques were used. For example, the lithiation/de-lithiation kinetics were determined for the anode and the cathode at low temperature

by conducting Tafel polarization measurements of the MCMB-Li<sub>x</sub>Ni<sub>y</sub>Co<sub>1-y</sub>O<sub>2</sub> cells in contact with the various electrolytes. When the kinetics of the anode and cathode are compared at low temperature for the two cells previously described, as shown in Fig. 9, it is apparent that significant differences are observed between the two cells.



**Fig. 9.** Tafel polarization curves of LiNiCoO<sub>2</sub> electrodes (1 and 2) and MCMB electrodes (3 and 4) in contact with different electrolytes at -20°C.

When measurements of the cell containing the low EC-content temperature electrolyte were performed at -20°C, it is apparent that anode kinetics are superior to that of the cathode with higher current densities being able to be sustained. Whereas, when the cell containing the high EC-content electrolyte was measured, the anode polarization effects were observed to be poorer than that of the cathode. These results support the contention that the relative electrode kinetics at low temperature can greatly influence the likelihood of lithium plating, suggesting that poor anode kinetics (or alternatively, excellent cathode kinetics) can contribute to the anode being preferentially (and undesirably) polarized upon charging at low temperature.

## Conclusions

The low temperature charge and discharge characteristics have been investigated in experimental MCMB-LiNiCoO<sub>2</sub> cells. Excellent discharge characteristics have been observed down to temperatures as low as -40°C using low EC-content multi-component electrolytes. The electrolyte type has been observed to greatly influence the charge characteristics at low

temperature. Under certain conditions, evidence of lithium plating has been observed and has been seen to be facilitated by high charge voltage, high charge currents, and undesirable electrode kinetics.

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